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ILLINOIS UNIV AT URBANA DEPT OF CHEMISTRY  
CHEMILUMINESCENCE FROM THE REACTION OF 2-METHYLENE-3-ACETYLOXAZ-ETC(U)  
AUG 82 D STEFFEK; R C MEBANE; G B SCHUSTER N00014-76-C-0745

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The reaction of 2-methylene-3-acetyloxazoline-4,5-dione (1) with hydrogen peroxide in the presence of a fluorescent aromatic hydrocarbon generates light. The mechanism for light generation was investigated and found to parallel that of oxalate esters. The reaction of dione (1) is catalyzed by added base, but the chemiluminescence intensity drops as the base concentration increases. A reaction sequence is proposed consistent with the experimental observations.		

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Chemiluminescence from the Reaction of 2-Methylene-3-acetyloxazoline-  
4,5-dione with Hydrogen Peroxide

by

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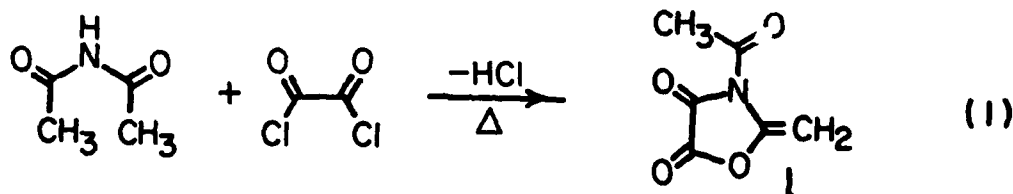
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Chemical reactions that generate visible light have been actively investigated for the past 50 years.<sup>1</sup> Recent research has revealed important details of the chemical and physical transformations required for efficient light generation from these processes.<sup>2</sup> Typically these reactions involve, as starting material or as a key intermediate, an organic peroxide. Conversion of the weak oxygen-oxygen bond of the peroxide to a much stronger carbon-oxygen double bond in a product carbonyl group in most cases supplies much of the energy required to form the requisite electronically excited state. The mechanism for conversion of the chemical potential energy of the peroxide to visible light depends on the details of the structure of the peroxide. One of the most efficient chemiluminescent systems yet discovered is based on the reaction of hydrogen peroxide with certain derivatives of oxalic acid in the presence of a suitable fluorescer.<sup>3,4</sup> This reaction can generate light with an efficiency approaching 35%,<sup>5</sup> and forms the basis for the popular Cyalume light sticks. For these reasons we were attracted to the recent report by Richter and Temme<sup>6</sup> of a new reaction of aliphatic imides with oxalyl chloride to give oxazolidinediones, eq 1. We set out to examine the possibility that these "derivatives" of oxalic acid are capable of generating light. Herein we report the results of that investigation.



Oxazolidinedione **1** was prepared according to the published procedure.<sup>6</sup> When a solution of dione **1** in dimethylphthalate containing 9,10-diphenylanthracene (DPA) is treated with hydrogen peroxide blue chemiluminescence characteristic of DPA fluorescence can be easily seen in a darkened room

with the unaided eye. Control experiments showed that all three ingredients are required to generate light. Thus the central question asked at the outset of this investigation can be answered in the affirmative. Dione  $\lambda$  is capable of generating chemiluminescence. We set out next to explore the details of the chemical transformations leading to light.

The rate of the chemiluminescent reaction of  $\lambda$  is increased by added bases. We explored several potential catalysts for the reaction of  $\lambda$  with hydrogen peroxide and found that 2,6-lutidine gives clean and reproducible results. Addition of the lutidine to the reaction mixture has two effects on the chemiluminescent process. First, as the lutidine concentration is increased the observed pseudo first-order rate of decay of the chemiluminescent reaction increases, Figure 1. Second, increasing the lutidine concentration from  $5.2 \times 10^{-4} \text{ M}$  to  $5.2 \times 10^{-2} \text{ M}$  leads to a decrease in the total chemiluminescent intensity obtained by a factor of about 15. Thus the lutidine must be effecting two parts of the reaction that leads eventually to light. The lutidine increases the rate of the slow step while inhibiting eventual generation of light. It should be noted that while lutidine does quench the fluorescence of DPA in dimethylphthalate this process alone is not sufficient to account for the decrease in light intensity.<sup>7</sup>

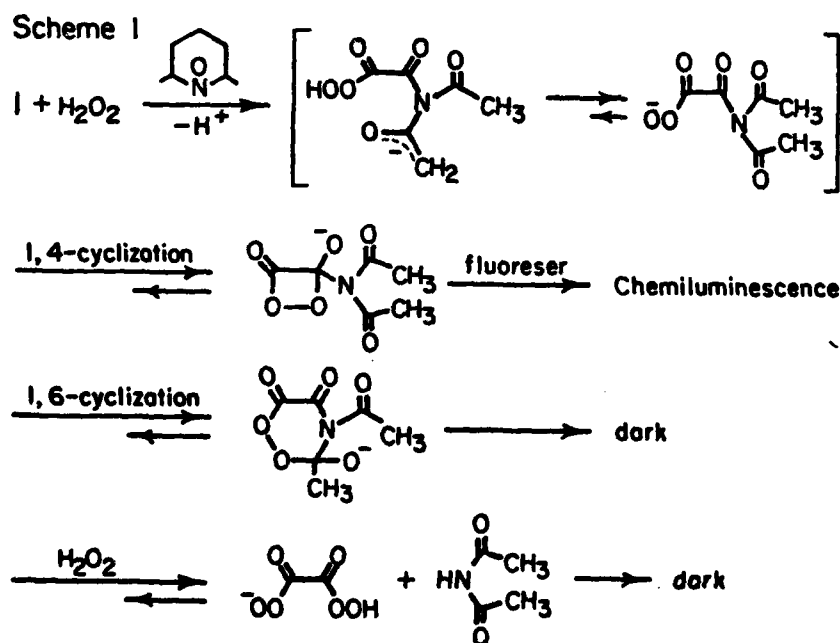
In a similar fashion we examined the effect of hydrogen peroxide concentration on the rate of the chemiluminescent reaction of  $\lambda$  and its light generating efficiency. This study revealed that the hydrogen peroxide and the base have parallel effects. Increasing the hydrogen peroxide concentration increased the rate of reaction while simultaneously decreasing the light output.

Changing the fluorescer structure reveals some additional details about the light generating process. The aromatic hydrocarbon fluorescers such as DPA, rubrene, perylene and 9,10-diphenylethynylanthracene all give

reasonably intense chemiluminescence. However, 9,10-dibromoanthracene (DBA), which has been shown to be a useful diagnostic for the generation of triplet excited states,<sup>8</sup> gives no meaningful light above the low background level. This observation, similar to one we made earlier for diphenoyl peroxide chemiluminescence,<sup>9</sup> is indicative of the operation of the chemically initiated electron-exchange luminescence (CIEEL) mechanism.<sup>2</sup>

Investigations of the chemiluminescence of some other oxalic acid derivatives has revealed that the fluorescer catalyzes the decomposition of a metastable intermediate.<sup>4</sup> Thus addition of the fluorescer to the reaction mixture some time after the other reagents have been mixed still yields nearly as much light as is obtained when the fluorescer is present from the outset. Similar attempts to detect a metastable intermediate from dione **1** were unsuccessful. Late addition of the fluorescer did not generate any light above that expected based on the known rate of reaction of the system components.

The results of these investigations permit us to suggest, as a working hypothesis, the mechanism for the chemiluminescence of dione **1** shown in Scheme 1. This mechanism is modeled after a similar proposal made by



Rauhut for the chemiluminescence of oxalate esters.<sup>4</sup> In the first, and rate-limiting, step hydroperoxide anion adds to the oxazolidione opening the ring to generate first an enolate anion and then the peroxy-carboxylate anion. The rate of this reaction should be sensitive to the lutidine concentration since it depends upon the amount of hydroperoxide present. The fate of the ring opened intermediate probably determines the chemiluminescence yield. Three reasonable alternative reactions are suggested; 1,4-cyclization leading to a dioxetane intermediate is the most likely route to the observed chemiluminescence, 1,6-cyclization, and base catalyzed addition of a second equivalent of hydrogen peroxide, can compete with the dioxetane route and do not lead to light. The base catalysis of the reaction rate and inhibition of chemiluminescence are consistent with this proposal. Also, the absence of a metastable intermediate is reasonably accounted for since reversal of the 1,4-cycloaddition gives the dark routes another opportunity to consume the intermediate.

We have qualitatively measured the light generating efficiency of the reaction of  $\frac{1}{\nu}$  and find it to be several orders of magnitude less than the most efficient oxalate esters. However, no attempt has yet been made to optimize the structure of the oxazolidione to increase light output.

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## Experimental Section

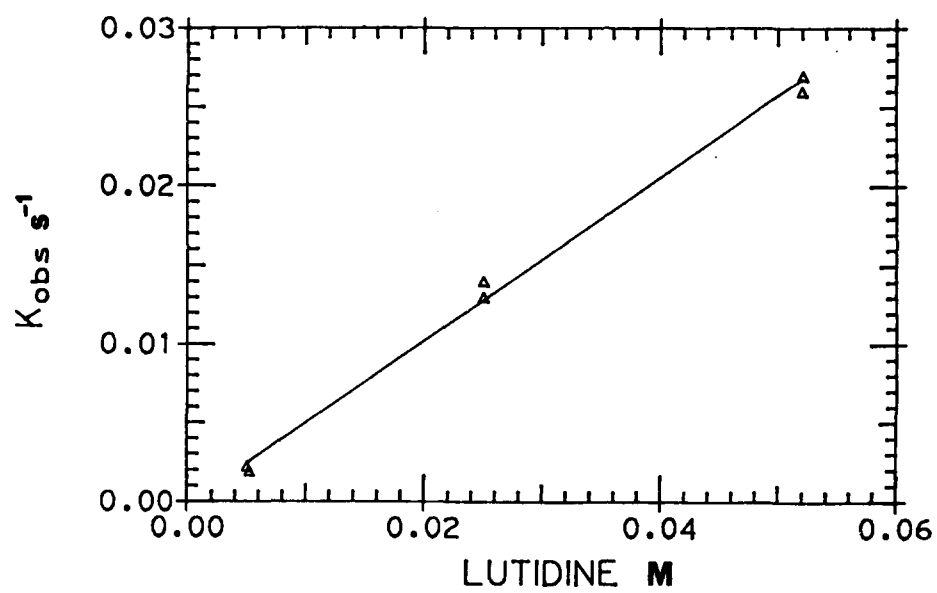
General. Solvents were purified by distillation before use. Fluorescers were chromatographed on alumina and then recrystallized. The chemiluminescence measurements were performed by the photon counting method at room temperature using the apparatus previously described.<sup>10</sup>

Typical chemiluminescence measurement. A solution of oxazolidione 1 in dimethylphthalate was added to a solution of the fluorescer and hydrogen peroxide, also in dimethylphthalate, so that the final volume was ca. 2.0 mL. Typical concentrations of these reagents in this solution were 1,  $5.5 \times 10^{-4}$  M; fluorescer,  $3.5 \times 10^{-4}$  M;  $H_2O_2$ , 0.4 M. For the lutidine catalyzed runs was the base also present in the peroxide solution. The light output from these solutions were monitored for ca. 4 half-lives at room temperature.



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Captions for Figure

Figure 1 The effect of added lutidine on the observed first order rate constant for decay of chemiluminescence from  $\text{I}_2$  in dimethylphthalate at room temperature. The catalytic rate constant is  $5.2 \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$ .

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